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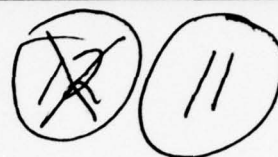


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ENVIRONMENTAL EFFECTS ON THE DEFORMATION OF POLYMERS
AT LOW TEMPERATURES

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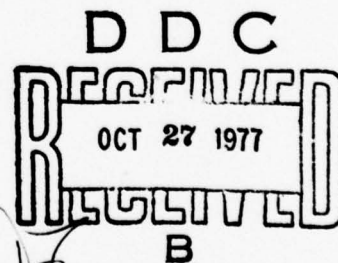


BY NORMAN BROWN

JUNE 15, 1977

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The mechanical properties of every linear polymer are affected by liquid and gaseous nitrogen, Argon, and oxygen if the temperature is less than about 70 degrees above the boiling point. The tensile strength decreases and the creep rate increases with respect to an increase in the surface concentration of the gas. The surface concentration is related to the pressure and temperature by the parameter peQ/RT where Q was about equal to the heat of vaporization of the gas. The usual effect of the gas was to produce crazes. About 12 gases were tested		

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Abstract (continued)

and the only two gases that had no effect were helium and hydrogen because they have low heats of vaporization. The range of the experiments were from 78K to the glass transition temperature. The mechanical behavior was also found to depend on the size and shape of the specimen as measured by area per unit volume because crazes usually nucleate at the surface. It was found that the macroscopic mechanical behavior could be quantitatively derived from the measureable microscopic parameters of the crazes. The pressure range of 0-1 atmospheres was investigated.

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FORWARD

The fact that a supposedly inert gas such as argon or nitrogen could produce crazes was originally discovered by Mark F. Parrish and myself during the course of his Ph.D. research. The effect was first reported in March Meeting of the American Physical Society at Atlantic City in 1972. Since every polymer that was exposed to N_2 at low temperatures crazed and/or had its tensile strength affected, it meant that all the existing low temperature observations on the strength of polymers did not represent the intrinsic behavior of the material. Therefore it was one of the major purposes of this research program to exhibit the intrinsic strength of polymer. Since helium was found to act as an inert environment like vacuum, it is generally used. A significant difference between the intrinsic strength of polymers at 78K and their strength in N_2 was observed in all cases. Usually liquid nitrogen reduces the intrinsic tensile strength about 25% when crazing occurs.

Another major purpose of the research was to determine the basic mechanism for the phenomenon. The reason why a gas such as argon interacted with a polymer is based on the fact the gas and the polymer have in common the Van der Waals bond. It is this bond which resists the deformation of unoriented polymers. The gas simply weakens this bond at points of stress concentration so that the craze forms.

It was observed that in gaseous environments the strain rate had a much greater effect on the yield point than in an

inert environment. The first theory on the growth of crazes in gaseous environments assumed that the diffusion of the gas into the polymer was the rate determining process. However, subsequent quantitative experiments on the effect of gas pressure on the velocity of crazes showed that the velocity was controlled by the rate of deformation required to produce the fibrillation that constitutes the craze.

This research project contains the first data on the effect of gas pressure (0-1 atmosphere) on the stress-strain and creep behavior of polymers. The gaseous environment has the advantage over liquids for studying environmental crazing because the surface concentration of the crazing agent can be precisely controlled. It was interesting to show that as little as 0.05 atm. of N_2 at 78K could produce a measureable change on the deformation behavior of a polymer.

There are areas still to be explored such as the effects of higher gas pressures and the effects of the environmental gas on fracture and fatigue.

I would like to thank the Office of Army Research and particularly Dr. George Mayer for the opportunity to explore this fascinating area of research. Dr. Mayer was very cooperative and helpful during the course of the research.

Norman Brown
University of Pennsylvania
June 1977

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Summary of Significant Results

A. Stress-Strain Curves

The stress-strain curves of a large variety of linear polymers, both amorphous and highly crystalline were measured in a liquid and gaseous environments such as He, H₂, N₂, Ar, O₂, CO₂, CO, CH₄, H₂S, N₂O and CH₃(CH₂)₃CH₃ (isopentane) in temperature range of 78K to T_g and in the pressure range of 0-1 atmosphere. Except for He and H₂, one or more of the above environments had an effect on the tensile strength of every polymer that has been tested in this and other laboratories. Generally most tests have been conducted in N₂ because it is most convenient and in He because it acts inertly (like vacuum).

The N₂ environment usually reduces the tensile strength and produces crazes, but for some polymers, Nylon and [CH₂CCl₂]_n ("Saran-Wrap"), the tensile strength was increased relative to its value in He. This latter effect is attributed to the blunting of points of stress concentration so that the brittle fracture stress is increased. Preconditioning of Nylon and [CH₂CCl₂]_n in N₂ under stress will increase the fracture strength even in a He environment.

The typical effect of the gaseous environment is to produce crazes and reduce the tensile strength or yield point as shown in Figure 1 with PMMA. Generally the effect of a particular gas on the tensile strength decreases with increasing temperature. For a given pressure, each gas has a temperature above which it has no effect on the tensile strength and it stops being a crazing

agent. The temperature range over which the gas is active depends primarily on the gas. For all polymers tested, N_2 becomes inactive above 150K at a pressure of 1 atmosphere. Some gases become ineffective with certain polymers at higher temperature because the polymer becomes ductile and prefers to deform by shear rather than by crazing. For example CO_2 will craze PMMA up to 260K but will not effect PTFE at 200K or above.

The temperature range over which a particular gas may be effective is determined by its heat of vaporization and by the pressure. In general, it was found that the effect of the gaseous environment on the tensile strength was given by an equation of the form

$$\sigma_c/\sigma(\text{inert}) = \{p \exp(Q/RT/p^*)\}^{-n}$$

where σ_c and $\sigma(\text{inert})$ are the tensile strengths in the gas and inert environment, p is the pressure, p^* , Q , and n are constants. Q is approximately equal to the heat of vaporization of the gas (Table 1) n depends primarily on the polymer and not the gas. For PC, PCTFE, and PMMA in a variety of gases n varied as 0.08, 0.1, and 0.13 respectively. Since the surface concentration of gases on polymers, varies as the factor $P e^{Q/RT}$, all the experimental data show that the surface concentration of the gas is an important factor in determining its effectiveness as a crazing agent.

The question of the difference in behavior between a gas and a liquid environment was investigated. In the neighborhood of the boiling point, it made no difference whether the liquid or the gas was in contact with the polymer. Similarly in the

TABLE 1

GAS	HEAT OF VAPORIZATION (cal/mol)	Q FROM MECHANICAL TESTS (cal/mol)		
		PMMA	PS	PCTFE
N ₂	1335(a)	1270(creep)	1570(creep)	1570(creep)
		940(T.S.)	1460(T.S.)	1270(T.S.)
Ar	1500(a)	1020(T.S.)		1470(T.S.)
O ₂	1630(b)	1030(T.S.)		1520(T.S.)
CH ₄	1950(b)		1770(T.S.)	1780(creep)
O ₂	6030(a)	4050(T.S.)		5450(T.S.)

T.S. = Tensile Strength

(a) Thermodynamic Function of Gases, (Ed. F. Din), Butterworth, London, 1962

(b) O. Kubaschewski and E. Evans, "Metallurgical Thermochemistry", 3rd Edn., Pergamon, London, 1958

neighborhood of the sublimation temperature or of the freezing point, the state of the environment whether liquid, solid, or gas was not important in itself. However in a single phase gaseous environment, the effect of the environment decreases as the temperature increases. In a two phase environment liquid-vapor, or solid vapor, the effect of the environment decreases as the temperature decreases. Note the curve EFH in Figure 1. Figure 2 shows the effect of liquid isopentane as a function of temperature. Hiltner, Kastelic, and Baer² showed similar behavior for N₂ below its boiling and freezing point. The explanation for the difference in behavior of the single phase and two phase environment is as follows: for the single phase gas environment, decreasing the temperature increases the concentration of gas that adsorbs on the surface and therefore increases the amount of gas that can diffuse into the polymer. For the two phase system the surface of the polymer is completely saturated at all temperatures. However, as the temperature decreases, the amount of environmental agent that diffuses into the polymer decreases as the temperature decreases because the diffusion coefficient decreases. In the case of the single phase of gas the diffusion coefficient also decreases as the temperature decreases. However the amount of gas that permeates the polymers more strongly depends on the surface concentration. Obviously, if there were no gas on the surface, the diffusion effect could not be a factor.

B. Creep Curves

Crazing can be investigated in greater detail by means of creep curves than by stress-strain curves because during creep the stress is constant. The relationship between stress and the strain rate associated with crazing is determined by three factors (1) the number of crazes, (2) the growth rate of a craze, and (3) the size of a craze. The stress level controls the number of crazes and their growth rate. For a given stress level, the number of crazes that nucleate in a low temperature do so in a relatively short time. Thus during the stress-strain experiment at constant strain rate, as the stress increases the number of crazes constantly increase and therefore the size distribution is less homogeneous because the crazes start growing at different times. For a creep test, the stress is applied quickly to a constant level. Except for a very short period at the beginning, the number of crazes is constant throughout the test; and they all grow at the same velocity so that their size is comparatively uniform. Thus, by counting the number of crazes and their size, the average velocity of the crazes can be determined from a creep test. Thus, the effect of the environment on the number of crazes can be separated from the effect on the craze growth.

Figure 3 shows typical creep curves in gaseous environments. The creep rate is observed to increase with time. The shape of the creep curve can be explained in terms of the following quantitative relationship which has been a guiding principle in the course of the research:

$$\epsilon = \rho \gamma b A$$

where ϵ is the strain from crazes; ρ is the number of crazes per unit area of the surface (all crazes nucleate at the surface); γ is the area per unit volume of the specimen; b is the average craze opening displacement, and A is the average area of a craze. Experiments⁹ indicate that the linear dimensions of a craze increases linearly with time so that it is expected that $A = K_1 v^2 t^2$ where K_1 is a rate constant and v is the linear velocity of a craze. If b also increases linearly with time, then

$$\epsilon = \text{constant} \times \rho \gamma v^3 t^3$$

The creep curves in Figure 3 very closely fit the above relationship.

In general the creep rate increases with stress and pressure as indicated by Figure 3a and b. However, the creep rate decreases with increasing temperature as shown in Figure 3c. This temperature effect is consistent with its effect on the tensile strength. As the temperature increases, the surface concentration of the gas decreases so that both the density and growth rate of crazes decreases with a corresponding increase in tensile strength or decrease in creep rate. The combined effect of pressure and temperature on the creep rate is shown in Figure 4. The creep rate is generally increased with the same parameter, $p e^{Q/RT}$, which controls the tensile strength. The Q from the creep test is the same as that derived from the stress-strain curves. Values of Q are listed in Table I and show that Q is about equal to the heat of vaporization of the gas.

For most materials the creep rate usually increases with increasing

temperature because creep is controlled by the process of thermal activation. However, for crazing in a gaseous environment the creep rate is governed by two temperature dependent processes, (1) adsorption and (2) thermal activation. If the temperature is sufficiently high relative to the boiling point of the gas then the thermally activated process will dominate and the creep rate will increase with increasing temperature. Figure 5 shows the transition from adsorption controlled behavior to thermally activated control.

An indication of the dependence of the creep rate on the surface concentration of gas can be obtained from measurements of the adsorption isotherms. Pierce⁴ has determined the number of surface layers of N_2 on graphite surfaces as a function of $p e^{Q/RT}$. Others^{5,6} have measured the coverage of various gas on various polymers. From these results it is possible to estimate our creep rate as a function of the surface concentration as shown in Figure 6. We note that it is the formation of the first surface layer that produces the greatest change in the creep rate.

C. Fundamental Mechanism for Crazeing in Gaseous Environments

The mechanism of crazeing should be divided into two parts:

- (1) the nucleation of crazes as indicated by the number of crazes
- and (2) the growth rate of the crazes.

1. Nucleation

All our observations are consistent with the results of all other investigations, that crazes are nucleated at points of stress concentration. In a homopolymer the points of greatest stress concentration are usually at the surface of the material. A craze then nucleates at a stress concentrator at a stress level that depends on the severity of the stress concentration and on the intrinsic crazability of the given polymer. The stress level for crazeing depends on the temperature since the intrinsic strength of the polymer increases with decreasing temperature and on the surface concentration of the gas. Figure 7 shows the surface density of crazes as a function of the parameter $p e^{Q/RT}$. The surface density also depends on the surface density of defects at which the crazes nucleate. Experiments, whereby the surface roughness was changed, changed the density of crazes for a given stress and environment.

It is noteworthy that the density of crazes varies nearly linearly at low pressure with the surface concentration parameter $p e^{Q/RT}$. Thus, theories and our data suggest that the stress, σ_c , to nucleate a craze at defect which concentrates the stress by a factor q in a polymer whose intrinsic strength $\sigma(\text{inert})$ and in gaseous environment of pressure p and temperature T is given by

$$\sigma_c = \frac{\sigma(\text{inert}) \text{ constant}}{q p e^{Q/RT}}$$

where the constant depends on the softening of the polymer per unit of gas pressure. Thus, the number of crazes at a given level of applied stress will depend on the number of defects whose q is equal or greater than the value given by the above equation. The data and the above equation lead to the conclusion that number of defects with a given q increases as q decreases. This is expected because the smaller the defect the lower q and we expect the number of defects of a given size to increase with decreasing size.

2. Growth

The effect of the surface concentration factor $p e^{Q/RT}$ on growth rate or craze velocity was investigated on a single specimen with a fixed number of crazes. The effect of craze size was normalized so that the effect of $p e^{Q/RT}$ on the growth rate could be obtained as shown in Figure 8. The important feature of Figure 8 is that at a low p , log velocity varies linearly with p . This important observation permits us to make a very important conclusion concerning the mechanism of craze growth in a gaseous environment.

In an earlier theory of crazing in gaseous environments, it was assumed that the velocity of a craze was controlled by the diffusion of the gas into the polymer and that the applied stress merely acted to increase the diffusion coefficient. Based on this model the craze velocity was given by

$$V = \text{constant } p e^{Q/RT} D_0 e^{-(Q_D - \sigma v)/kT}$$

where $p e^{Q/RT}$ is the surface concentration factor, D_0 is the pre-exponential factor in the diffusion coefficient; Q_D is the activation energy for diffusion of the gas into the polymer; σ is the stress, and v is an activation volume for diffusion. This equation makes two predictions which are not supported by experiment: (1) the velocity should vary linearly with $p e^{Q/RT}$ and (2) V should always increase with T because Q_D is generally larger than Q which turned out to be equal to the heat of vaporization.

A new model is proposed in which the rate controlling process is the rate of micro plastic deformation required to fibrillate the polymer into a craze. The gas increases the rate of plastic deformation by softening (plasticizing the polymer) but the gas is always fully available depending only on the surface concentration but not on diffusion. Thus we use the Eyring formulation to describe the rate of growth via a process of thermally activated plastic deformation. The craze velocity is now given by the following equation:

$$V = \text{constant} \times \exp[-(Q_p - k p e^{Q/RT} - \sigma v)/RT]$$

where Q_p is the energy of the barrier to plastic deformation; k is a constant; $p e^{Q/RT}$ is the surface concentration of gas. This model states that the energy barrier to the fibrillation process required for crazing is reduced by an amount that depends linearly on the surface concentration of the gas. This equation leads to a linear dependence of $\log V$ on $p e^{Q/RT}$ as observed and also predicts the inversion of creep rate with temperature as demonstrated

by Figure 5. Thus, it is concluded that the deformation process associated with fibrillation is the rate limit process during the growth of crazes in a gaseous environment at low temperatures and that the amount of gas required for the process is determined by the surface concentration of the gas.

D. Relationship of Micro-parameters to Macroscopic Behavior

The basic equation

$$\epsilon = \rho \gamma b A$$

provides the fundamental bases for relating the microscopic characterization of crazing to the microscopic properties. First it is important to show that this basic equation is correct.

The creep strain was measured under many different conditions, and the micro-parameters ρ , b , and A were measured. The experimental value of strain was then compared with the value obtained from the equation. The results for PCTFE and PMMA are shown in figures 9 and 10 and verify the static aspect of the basic equation.

The dynamic aspects of the equation are determined by the stress and time dependence of ρ , b , and A . It was demonstrated in a previous paper how the stress-strain curve, and the creep curves could be calculated. The basic equation also predicts that the macroscopic behavior depends on the geometry and size of the specimen given by γ the surface to volume ratio; this is so because crazes nucleate at the surface. Experiments¹¹ were done to measure the effect of γ on the stress-strain behavior and on the stress-relaxation curve. It was found in accordance with the equation that specimens with the smaller diameter relaxed faster and have a lower yield if crazing is the prominent mode of deformation. The variation of γ with yield point is shown in Figure 11.

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$$\frac{2(z+w)}{z+w} = \gamma; 0.9a_f = b \quad lp = A$$
10. Same as fig. 9 except $0.7a_f = b$ and for PMMA

II. Publications Supported by the Research Grant

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"The Relationship of Creep, Recovery and Fatigue in Polycarbonate", with M.J. Mindel, Norman Brown, Journal of Materials Science 9, 1661-1669 (1974).

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III. M.S. Thesis University of Pennsylvania (1977)
by Bruce Metzger

ENVIRONMENTAL CRAZING OF AMORPHOUS
POLYMERS AT LOW TEMPERATURES

ABSTRACT

The intrinsic tensile behavior of polymers is altered by environments in certain specified conditions. In the present study, the crazing of polymethyl methacrylate, polystyrene, polycarbonate, and polychlorotrifluorethylene was studied under various gaseous environments: argon, helium, nitrogen, isopentane and methane. The mechanical testing of the polymers was performed at temperatures greater than or equal to the boiling points of the gases, except for isopentane which was used in its liquid region. The increase of strength of the polymers as the temperature of the gas increases and as its pressure decreases, was of main interest. Stress-strain and creep tests were performed on sheet specimens. The nucleation and growth of crazes was studied as a function of temperature, pressure, and stress for various gas-polymer systems. Environmental crazing behavior can be predicted from a knowledge of the effects of the individual variables.

The microstates of the crazed specimens such as craze density, length of crazes, craze penetration, and opening distance of crazes were all combined to calculate a macrostate of a total

crazed specimen. From individual craze strains a total strain due to crazing can be calculated. Appendix I derives Brown's equation $\epsilon_c = \frac{20 A b}{Z}$ ¹, equating all of the micro features with total strain. This can be compared with the experimentally recorded total strain. Craze velocities and heats of sorption which govern the rate of craze nucleation and craze growth were also determined.

The weakening of the Van der Waals bonds in linear polymers leads to the formation and growth of crazes. The interaction of the gas molecules with the surface and bulk of the polymer (both adsorption and absorption) causes this weakening effect². With a knowledge of craze velocities and sorption energies the craze nucleation and craze growth can be better understood. This knowledge of craze growth makes it possible to determine deformation rates and fracture criteria under the varying conditions of stress, temperature, pressure, environment, and for different polymers.

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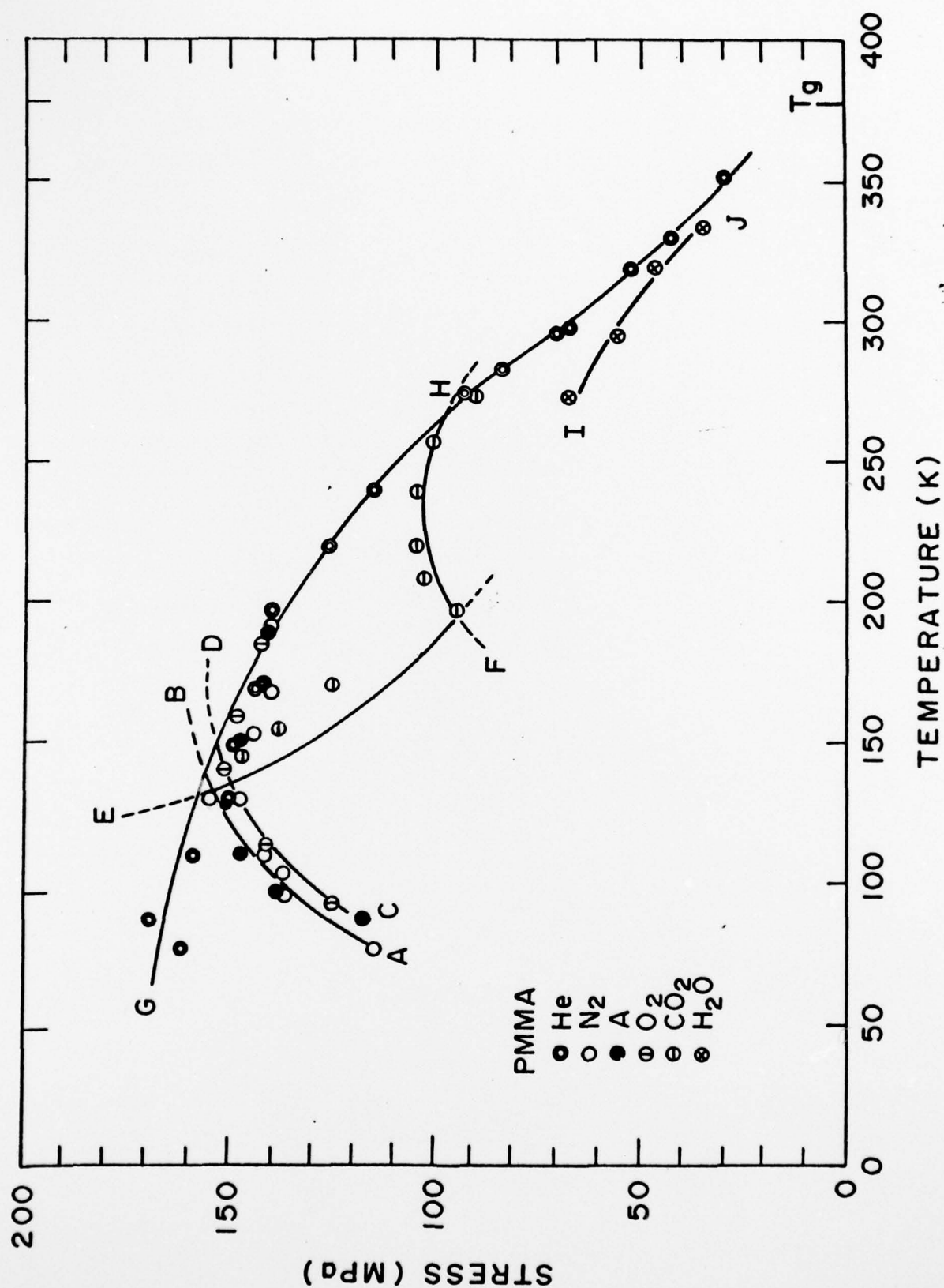


Figure 1

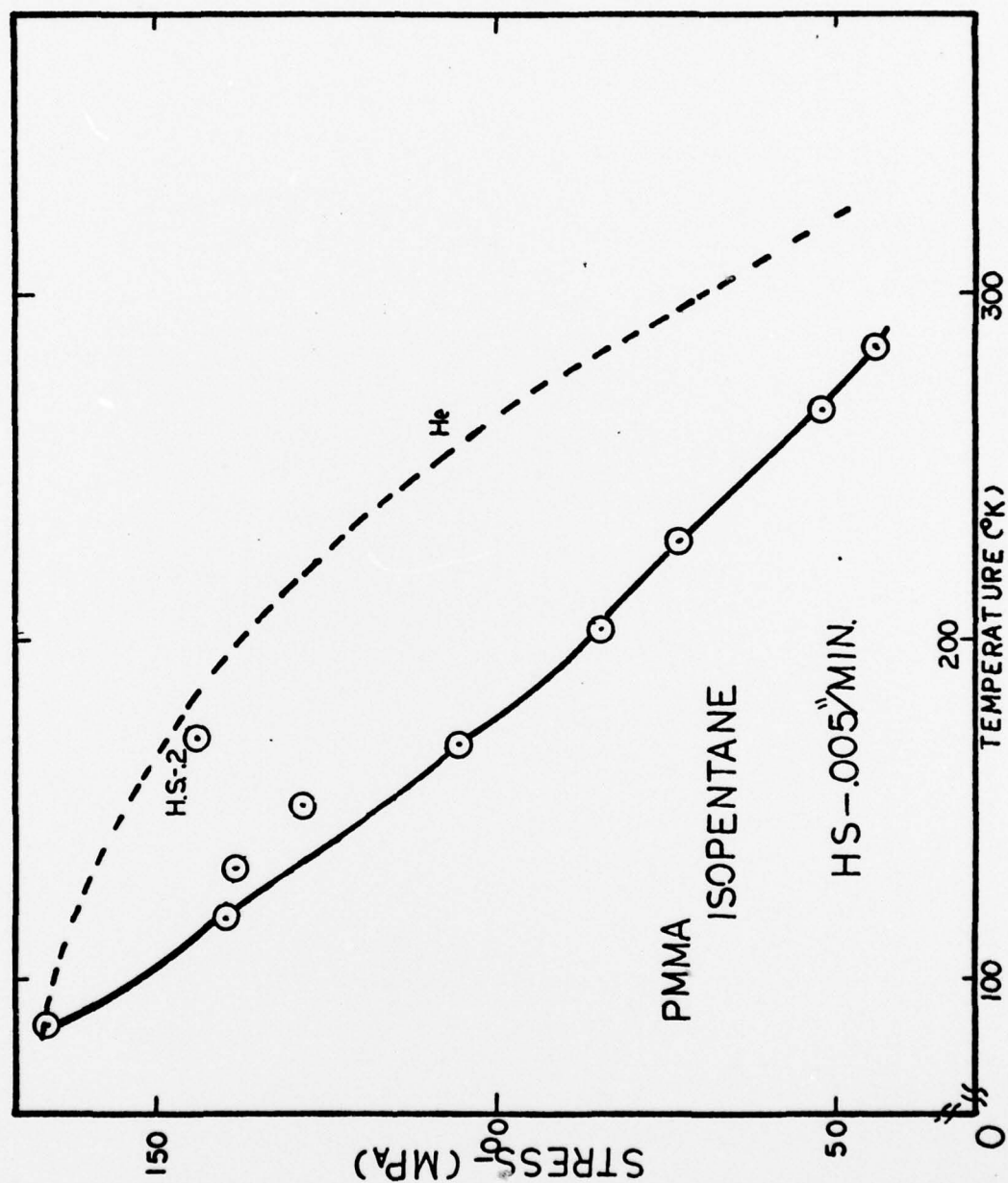


Figure 2 Tensile strength vs. temperature

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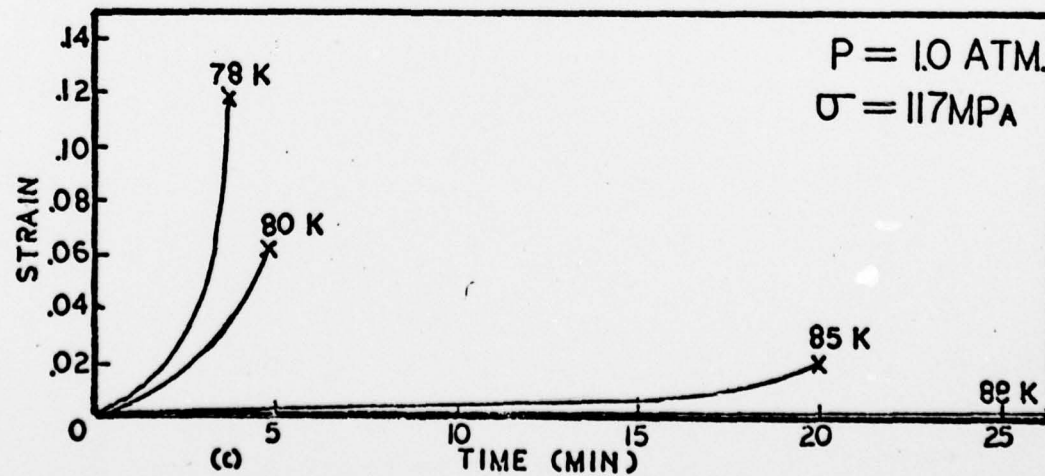
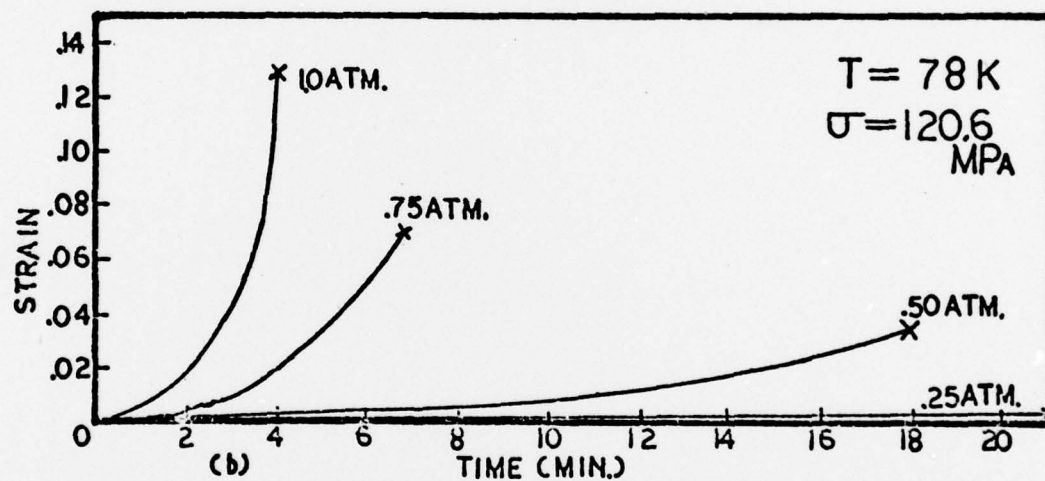
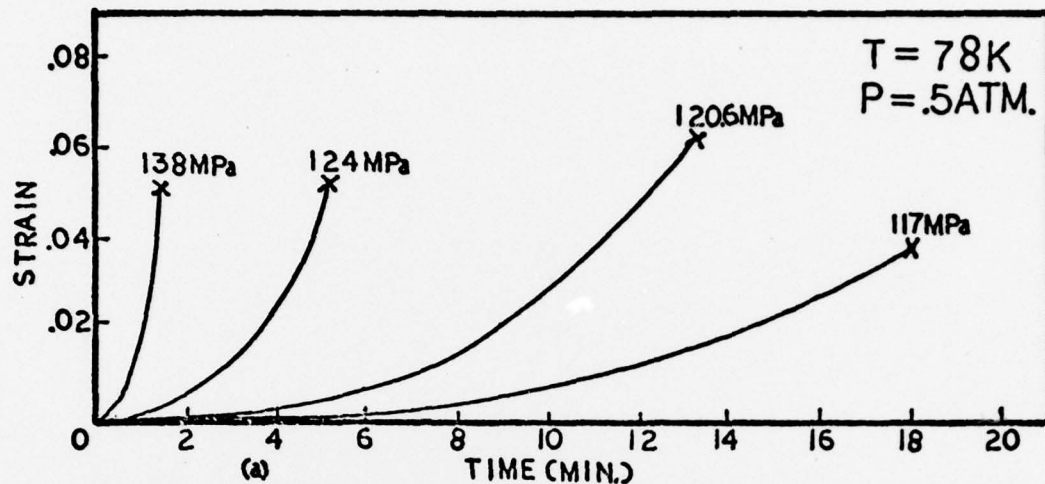


Figure 3

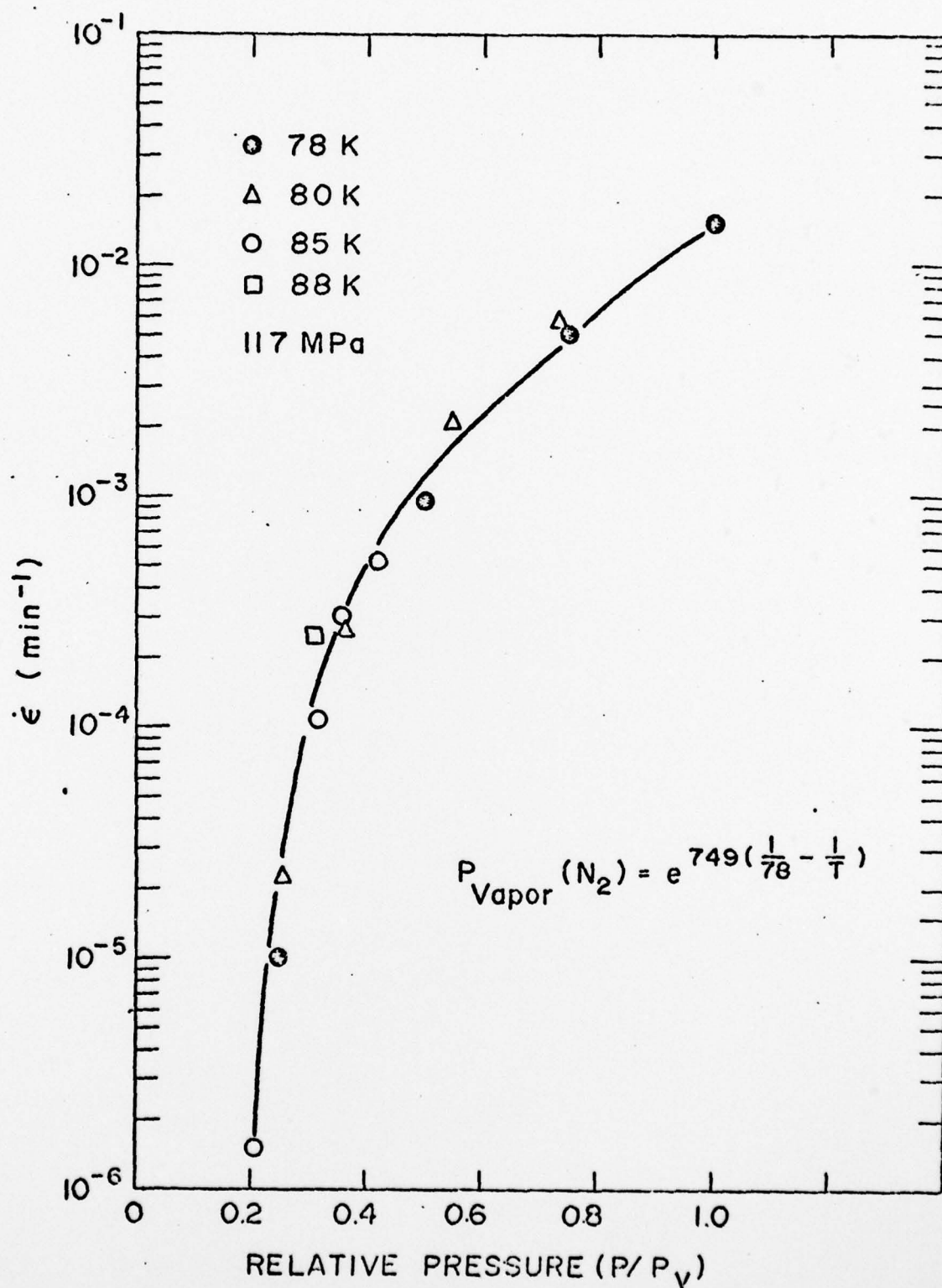


Figure 4 log strain rate vs. relative pressure

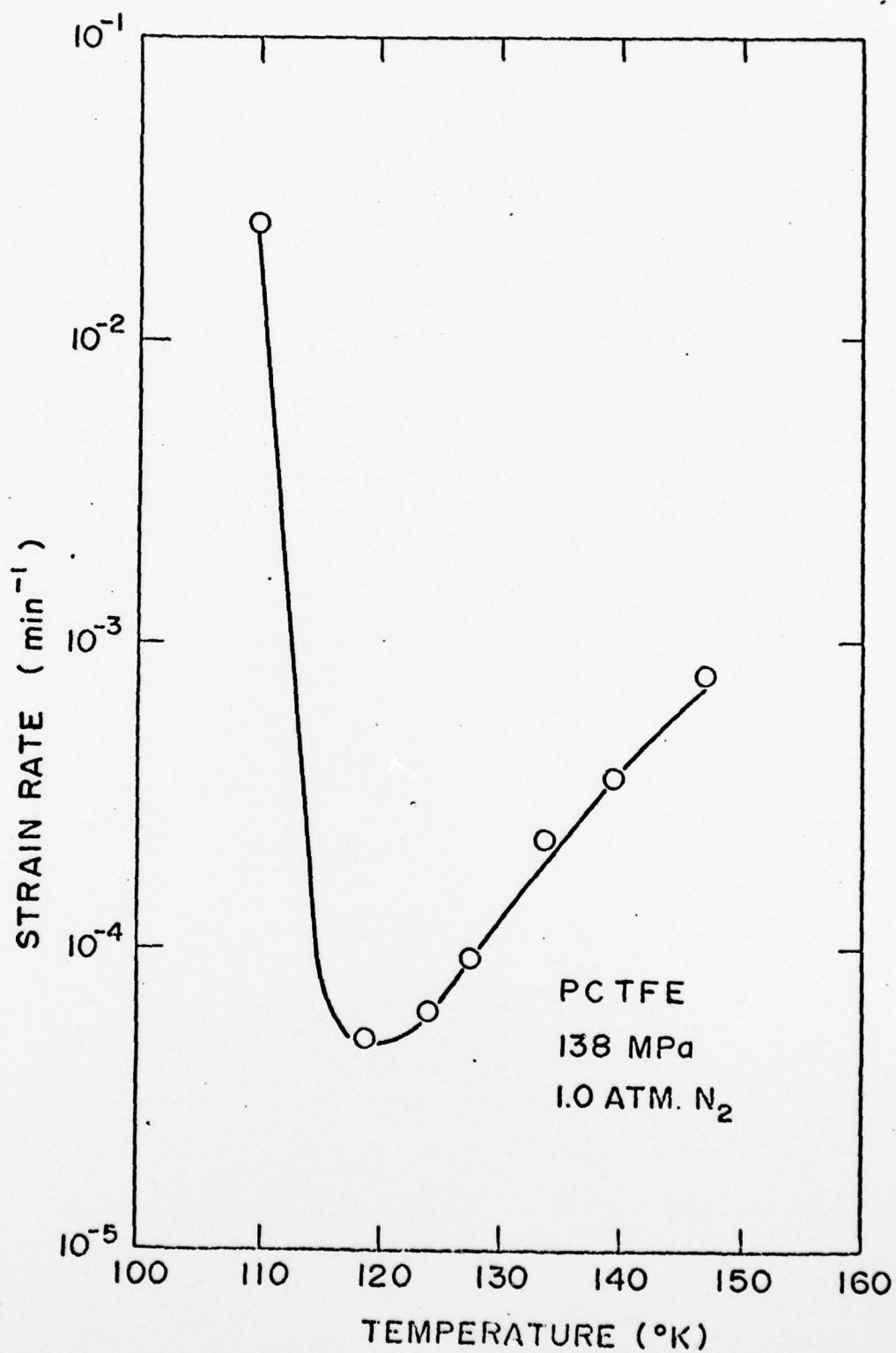


Figure 5 log strain rate vs. temperature

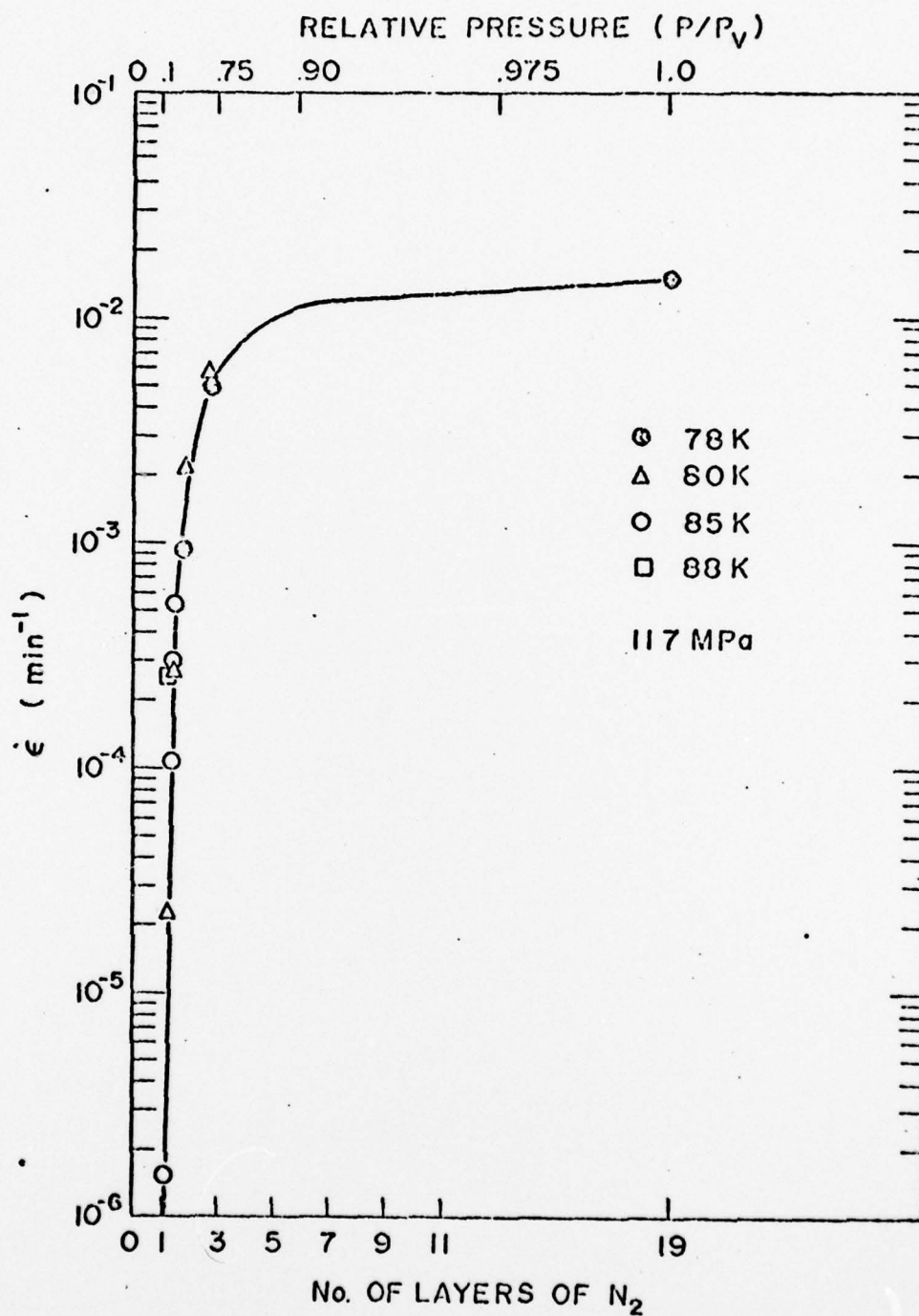


Figure 6 log strain rate vs. no. of layers of N₂

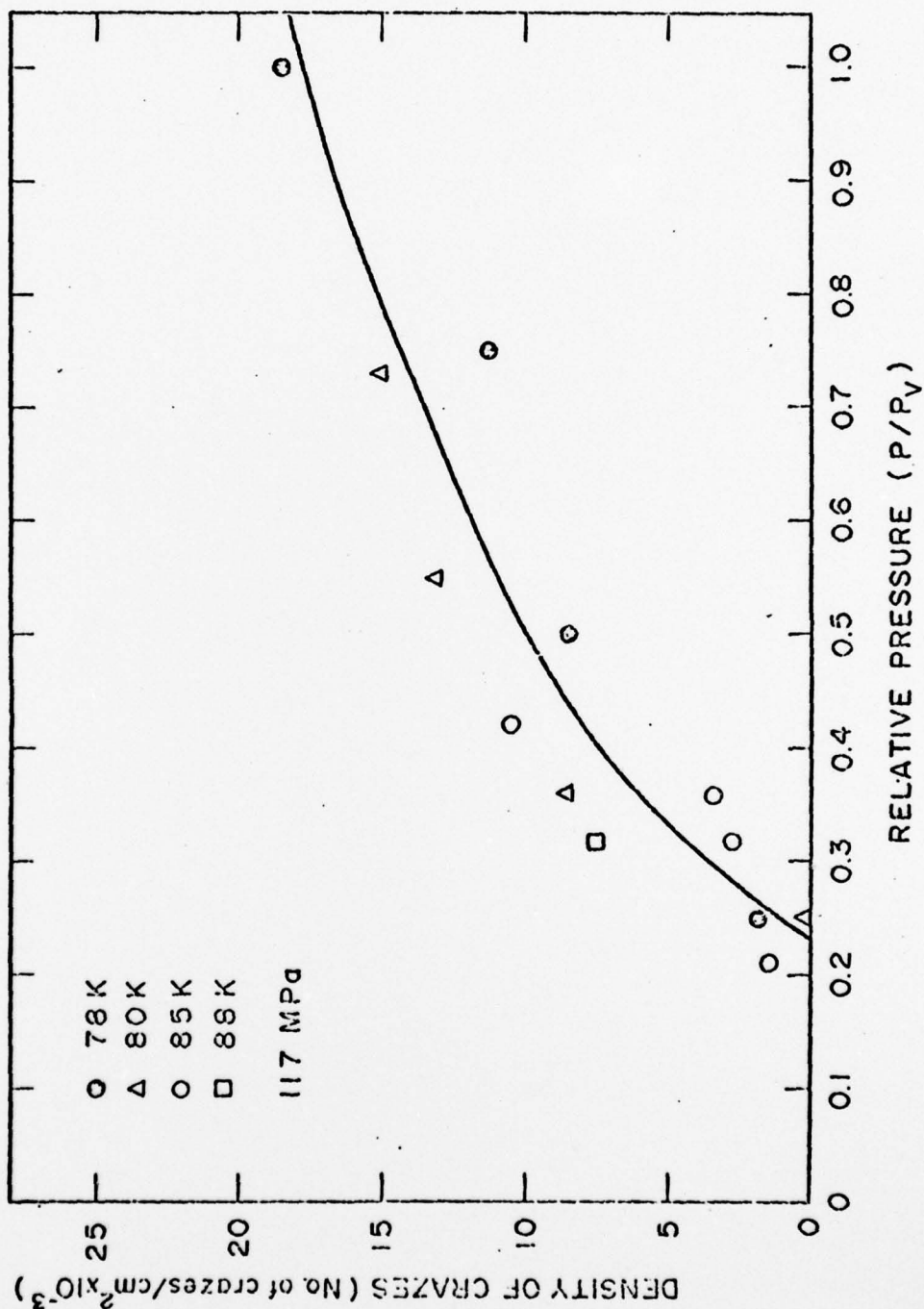


Figure 7 density of crazes vs. relative pressure for various temperatures

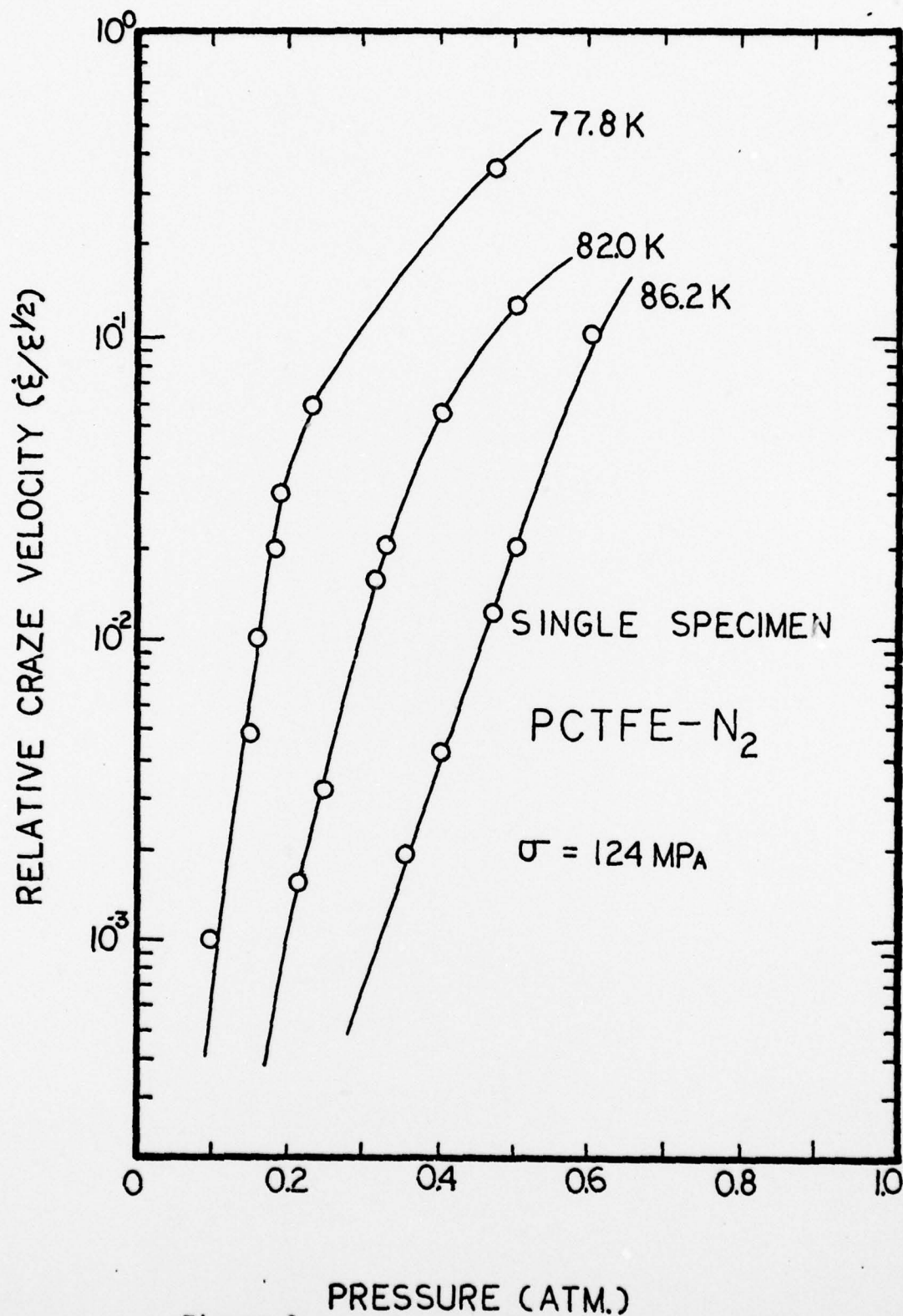


Figure 8

relative craze velocity vs. pressure

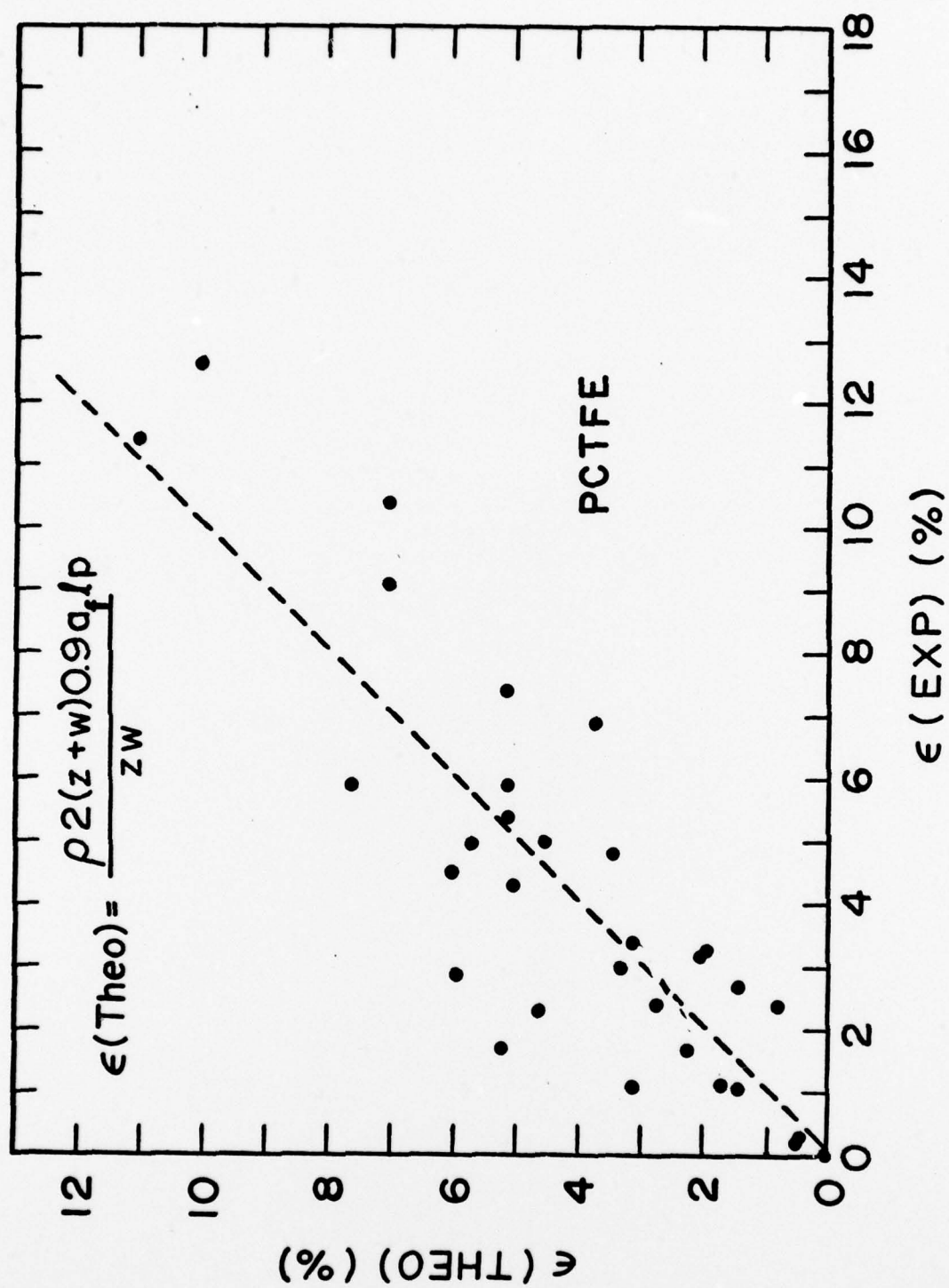


Figure 9

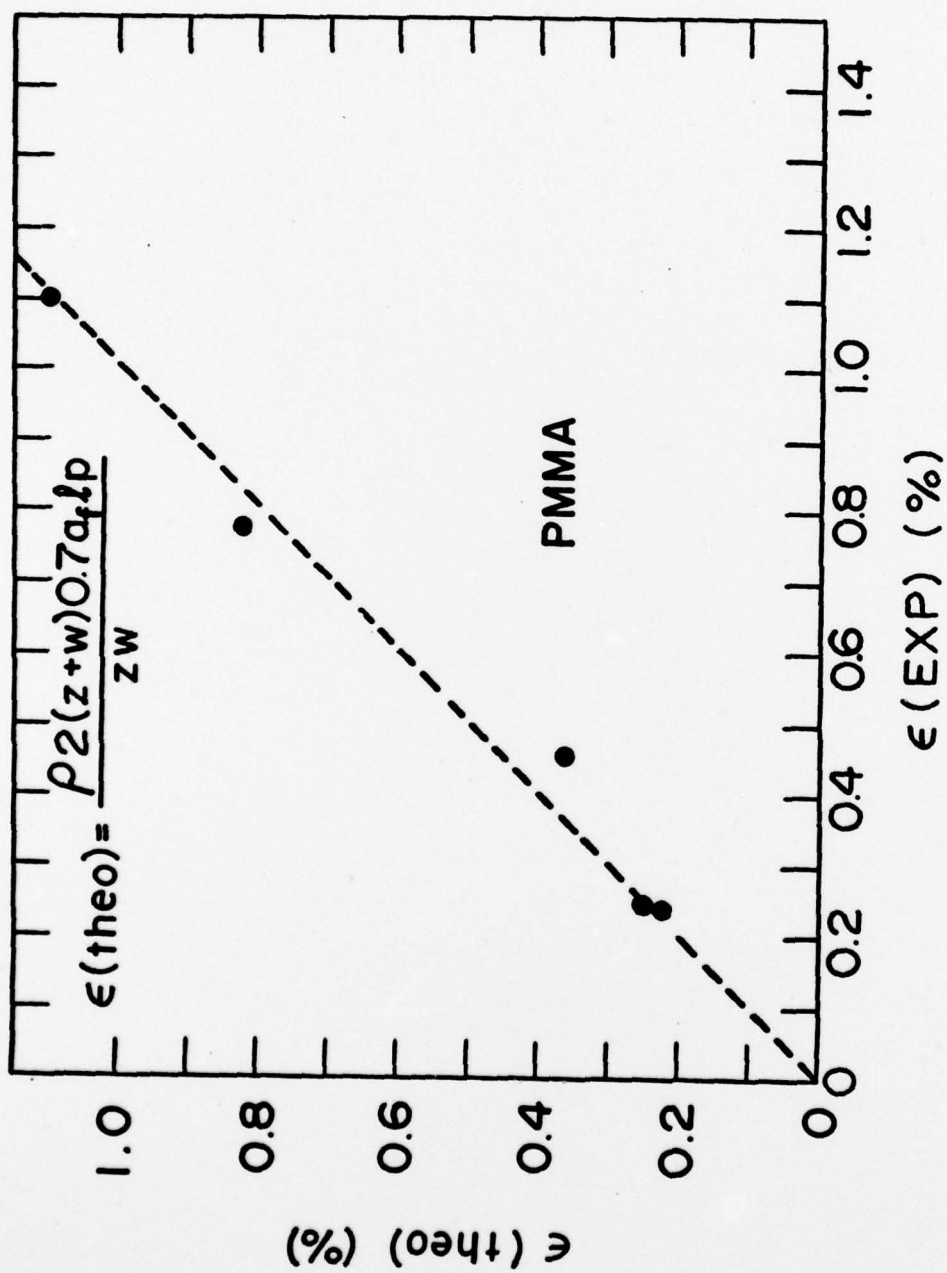


Figure 10

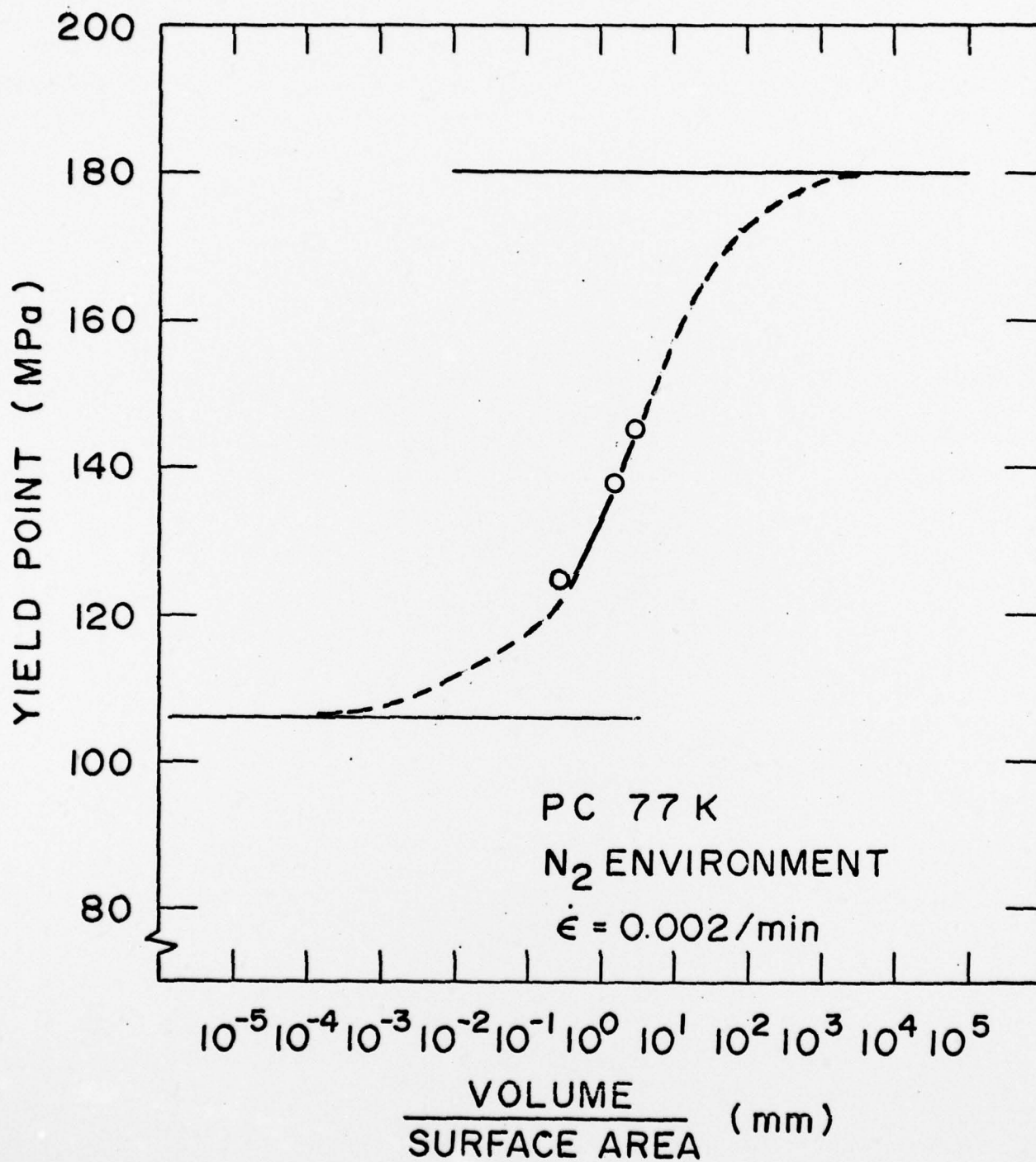
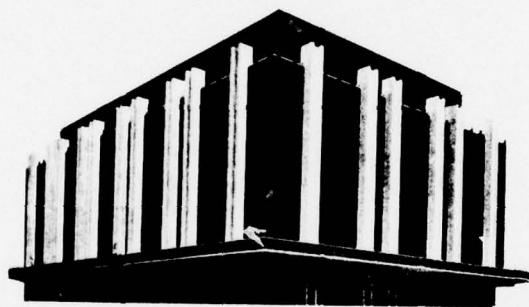


Figure 11



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